F-0316-US

VERIFICATION OF TRANSLATION

I, Michiyo AONO, of c/o Sudo International Patent Office, Shinyo Bldg. 6F, 6-1, Nihonbashi-Muromachi 1-chome, Chuo-ku, Tokyo 103-0022 JAPAN am translator of Japanese Patent Application No. 2002-240374 and I state that the following is an accurate translation to the best of my knowledge and belief.

(Signature of Translator) Michiyo Aono

(Dated) November 10, 2008

【Name of Document】 Specification

【Title of Invention】 Inorganic Compound Containing Active Oxygen and Process for Producing The Same

【Claims】

【Claim 1】 An inorganic compound that has an active oxygen developing mechanism and includes or occludes active oxygen, the inorganic compound including or occluding both a superoxide anion (O_2-) and a peroxide anion (O_2^{2-}).

【Claim 2】 The inorganic compound according to Claim 1, wherein the compositional formula of the aluminosilicate is $Ca_{12}(Al_{14-x}Si_x)$.

【Claim 3】 The inorganic compound according to Claim 2, wherein the compositional formula of the aluminosilicate is $Ca_{12}(Al_{14-x}Si_X)O_{33+0.5X}$, where the value of X is in the range of $0 < X \leqq 4$.

【Claim 4】 A method for manufacturing the inorganic compound according to Claim 1, wherein an aluminosilicate having an active oxygen developing mechanism is manufactured by heating hydrogarnet at no lower than 700°C and no higher than 1200°C.

【Claim 5】 The method according to Claim 4, wherein the compositional formula of the hydrogarnet is

$Ca_3Al_2(SiO_4)_{3-Y}(OH)_{4Y}$, where the value of Y is in the range of $0 \leqq Y < 3$.

【Claim 6】 An oxidation catalyst composed of the inorganic compound according to Claim 1.

【Detailed Description of the Invention】

【0001】

【Field of Industrial Application】

This invention relates to a method for manufacturing an inorganic compound including active oxygen, and more particularly relates to a novel active oxygen developing substance including or occluding both a superoxide anion (O_2^-) and a peroxide anion (O_2^{2-}), and to a method for manufacturing this substance, and applications therefor.

【0002】

【Prior Art】

An example of substances known and put to use in the past as active oxygen developing substances is a photocatalyst typified by titanium oxide. Electrons and holes are formed when light (UV rays) is absorbed by titanium oxide. Because the oxidative strength resulting from holes is greater than the reductive strength resulting from excited electrons with titanium oxide, adsorbed water on the catalyst surface is oxidized by the holes, producing hydroxy radicals (·OH). Meanwhile, a reaction proceeds in which the oxygen in the air is reduced, producing active oxygen (O_2^-). It is believed that active oxygen becomes water via hydrogen peroxide (H_2O_2) or the formation of a

peroxide of an intermediate of the oxidation reaction. There are also cases in which active oxygen acts directly on carbon-carbon bonds and decomposes harmful organic substances.

【0003】

Another substance known to develop active oxygen is a $12CaO \cdot 7Al_2O_3$ compound that encloses active oxygen species (Japanese Laid-Open Patent Application No.2002-3218). This $12CaO \cdot 7Al_2O_3$ compound is manufactured from a raw material mixture of calcium and aluminum in an atomic equivalent ratio of 12:14, which are subjected to solid phase reaction in a dry oxidative atmosphere controlled to an oxygen partial pressure of at least 10^4 Pa, and preferably at least 10^5 Pa, and a water vapor partial pressure of no more than 1 Pa, and at a high firing temperature of at least 1200°C, and preferably 1300°C. The active oxygen enclosed by a $12CaO \cdot 7Al_2O_3$ compound manufactured in an atmosphere in which the oxygen partial pressure and water vapor partial pressure are strictly managed, which requires a large quantity of thermal energy, is O_2^- and/or O^-.

【0004】

However, when it came to this type of active oxygen developing substance, no inorganic compound that would

include or occlude both a superoxide anion (O_2^-) and a peroxide anion (O_2^{2-}) was known up to now, and all that was known was the production of a superoxide with a $12CaO \cdot 7Al_2O_3$ compound or a photocatalyst such as the above-mentioned titania.

【0005】

【Subjects to be Solved by the Invention】

In light of the above situation, and the prior art discussed above, the inventors conducted diligent research aimed at developing a novel active oxygen developing substance that would be capable of including or occluding in its structure O_2^{2-} having greater oxidative strength than active oxygen species such as O_2^- and O^- known to be developed by photocatalysts such as titania or by a $12CaO \cdot 7Al_2O_3$ compound. As a result, they arrived at the present invention upon discovering that an aluminosilicate expressed by $Ca_{12}(Al_{14-X}Si_X)O_{33+0.5X}$ includes or occludes both a superoxide anion (O_2^-) and a peroxide anion (O_2^{2-}).

【0006】

It is an object of the present invention to provide a novel active oxygen developing substance that includes or occludes both a superoxide anion (O_2^-) and a peroxide anion

(O_2^{2-}), which are powerful oxidants, and a method for manufacturing the active oxygen developing substance.

It is another object of the present invention to provide a novel active oxygen developing substance wherein active oxygen such as O_2^{2-} is included or occluded in the structure of the substance.

It is another object of the present invention to provide an aluminosilicate which is a novel active oxygen developing substance that includes or occludes both a superoxide anion (O_2^-) and a peroxide anion (O_2^{2-}) in its structure.

【0007】

【Means for Solving the Subjects】

(1) An inorganic compound that has an active oxygen developing mechanism and includes or occludes active oxygen, the inorganic compound including or occluding both a superoxide anion (O_2−) and a peroxide anion (O_2^{2-}).

(2) The inorganic compound according to (1) above, wherein the compositional formula of the aluminosilicate is $Ca_{12}(Al_{14-x}Si_x)$.

(3) The inorganic compound according to (2) above, wherein the compositional formula of the aluminosilicate is

$Ca_{12}(Al_{14-X}Si_X)O_{33+0.5X}$, where the value of X is in the range of $0 < X \leqq 4$.

(4) A method for manufacturing the inorganic compound according to Claim 1, wherein an aluminosilicate having an active oxygen developing mechanism is manufactured by heating hydrogarnet at no lower than 700°C and no higher than 1200°C.

(5) The method according to (4) above, wherein the compositional formula of the hydrogarnet is $Ca_3Al_2(SiO_4)_{3-Y}(OH)_{4Y}$, where the value of Y is in the range of $0 \leqq Y < 3$.

(6) An oxidation catalyst composed of the inorganic compound according to (1) above.

【0008】

【The Aspect of the Invention】

The method of the present invention for manufacturing a novel active oxygen developing substance does not require control of the oxygen partial pressure or water vapor partial pressure, and the heating may be at a relatively low temperature of 1000°C or lower. An example of this manufacture will now be given, but the method of the present invention for manufacturing a novel active oxygen developing substance is not limited to just the following method. The

active oxygen developing substance of the present invention is manufactured by using hydrogarnet as a precursor substance, and heating it to at least 700°C in an electric furnace or the like under an air atmosphere. The chemical compositional formula of the hydrogarnet used as the precursor is $Ca_3Al_2(SiO_4)_{3-Y}(OH)_{4Y}$, where the value of Y is in the range of $0 \leqq Y < 3$.

【0009】

Meanwhile, the chemical compositional formula of the aluminosilicate having a novel active oxygen developing function is $Ca_{12}(Al_{14-X}Si_X)O_{33+0.5X}$, where the value of X is in the range of $0 < X \leqq 4$. The chemical composition when X = 4 is $Ca_{12}(Al_{10}Si_4)O_{35}$, and when $Ca_{12}(Al_{10}Si_4)O_{35}$ is synthesized, the composition of the precursor hydrogarnet is $Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8}$ (Y = 2.2). The hydrogarnet is synthesized as follows. First, a calcia source, an alumina source, and a silica source are mixed so as to match the hydrogarnet composition, that is, the composition of hydrogarnet with the desired Y value, and an excess of water is added to this to prepare a mixture.

【0010】

The calcia source here can be slaked lime, unslaked lime, calcium carbonate, gypsum, or the like; the alumina

source can be kaolin, alumina sol, boehmite, aluminum hydroxide, aluminum oxide, or the like; and the silica source can be kaolin, silica, amorphous silica, diatomaceous earth, silica sand, quartz, or the like. The prepared mixture is subjected to a wet heat treatment in an autoclave for at least 5 hours at a temperature of from 100 to 200°C to synthesize hydrogarnet. The reaction will not proceed adequately if the temperature is below 100°C, but too much thermal energy will be consumed if the temperature is over 200°C. The heating time can be shorter than 5 hours, but at least 5 hours is preferable in order to obtain hydrogarnet with good crystallinity.

【0011】

An aluminosilicate that is a novel active oxygen developing substance can be obtained by heating hydrogarnet to 700°C or higher and 1200°C or lower in an air atmosphere. Heating at a temperature under 700°C is undesirable because pyrolysis will be inadequate. The heating may be performed at an even higher temperature, but this will consume too much thermal energy, so the limit is set at 1200°C or lower. An aluminosilicate that is the novel active oxygen developing substance of the present invention can be obtained by heating hydrogarnet synthesized by the above

method. Cases in which $X = 4$ and $X = 2$ are given below as examples.

【0012】

The compositional formula of the precursor hydrogarnet used to synthesize $Ca_{12}Al_{10}Si_4O_{35}$ ($X = 4$) is $Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8}$ ($Y = 2.2$), and the pyrolysis thereof that occurs at 700°C is expressed as follows.

$$5Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8} \rightarrow Ca_{12}Al_{10}Si_4O_{35} + 3CaO + 22H_2O$$

The compositional formula of the precursor hydrogarnet used to synthesize $Ca_{12}Al_{12}Si_2O_{34}$ ($X = 2$) is $Ca_3Al_2(SiO_4)_{1/3}(OH)_{32/3}$ ($Y = 8/3$), and the pyrolysis thereof that occurs at 700°C is expressed as follows.

$$6Ca_3Al_2(SiO_4)_{1/3}(OH)_{32/3} \rightarrow Ca_{12}Al_{12}Si_2O_{34} + 6CaO + 32H_2O$$

【0013】

The $Ca_{12}Al_{10}Si_4O_{35}$, $Ca_{12}Al_{12}Si_2O_{34}$, and so forth obtained from the above reaction formulas are examples of aluminosilicates that are the novel active oxygen developing substance of the present invention. The novel active oxygen developing substance of the present invention is obtained within the range of $0 < X \leqq 4$, and is produced by the pyrolysis of hydrogarnet, which is a precursor thereof. As can be seen from the pyrolysis formulas, unslaked lime (CaO) is admixed as a by-product, but unslaked lime does not

participate in the development or inclusion of active oxygen. CaO can be easily removed by dissolving it with a dilute acid such as hydrochloric acid or nitric acid.

【0014】

ESR measurement and Raman spectroscopy are two ways to check whether or not the hydrogarnet pyrolyzate, that is, the aluminosilicate that is the novel active oxygen developing substance, includes or occludes active oxygen such as superoxide anions (O_2^-) and peroxide anions (O_2^{2-}). For instance, the results of ESR and Raman spectroscopy at room temperature for the $Ca_{12}Al_{10}Si_4O_{35}$ used in the working examples given below will now be described. First, Fig. 1 shows the ESR measurement results. The spectrum appearing at g_1 = 2.049 mT indicates the presence of superoxide anions. Fig. 2 shows the results of Raman spectroscopy at room temperature. Just as in ESR measurement, the presence of superoxide anions is confirmed from a peak at 1075 cm^{-1}.

【0015】

The results in both Figs. 1 and 2 tell us that $Ca_{12}Al_{10}Si_4O_{35}$ is included or occluded in the structure of the superoxide anions. Furthermore, Raman spectroscopy results for $Ca_{12}Al_{10}Si_4O_{35}$ reveal a distinct peak at 853 cm^{-1} as well as at 1075 cm^{-1}. The former corresponds to a peak originating in peroxide anions, and the latter in superoxide

anions. The above results lead to the conclusion that the novel active oxygen developing substance of the present invention includes or occludes superoxide anions and peroxide anions in its structure.

【0016】

Fig. 3 shows the crystal structure of $Ca_{12}Al_{10}Si_4O_{35}$. The structure of $Ca_{12}Al_{10}Si_4O_{35}$ is a cubic system, with a lattice constant of a = 12.0116 Å, and a space group of $I\bar{4}3d$. This is a zeolite-like structure in which $(Al,Si)O_4$ tetrahedra are formed in the form of a framework, and active oxygen O_2^- and O_2^{2-} are present in the voids (spaces of about 4 Å) in this framework.

【0017】

The active oxygen included or occluded by the aluminosilicate that is the novel active oxygen developing substance of the present invention is a powerful oxidant, is discharged from within the structure when heated to 400°C or higher, and participates in chemical reactions and so forth. In other words, the active oxygen included or occluded by the aluminosilicate that is the novel active oxygen developing substance of the present invention is able to move at a temperature of 400°C or higher. For instance, the novel active oxygen developing substance has the ability to

completely oxidize and decompose volatile organic compounds (VOCs) into CO_2 or H_2O at a low temperature of 400 to 600°C. Because of this, the active oxygen developing substance of the present invention can be used as the active component of an oxidation catalyst.

【0018】

The active oxygen in the structure is gradually consumed as an oxidative decomposition reaction continues under an oxygen-free atmosphere, and if the reaction continues long enough, the active oxygen is completely used up, after which no more is supplied. However, if air or oxygen is supplied to the novel active oxygen developing substance after active oxygen ceases to be supplied, active oxygen will be produced again in the structure and the powerful oxidizing action will be restored. This is a distinctive feature of this substance. Fig. 4 shows experimental results. Therefore, if air or oxygen is continually supplied during the oxidative decomposition of VOCs and the like, the supply of active oxygen from the novel active oxygen developing substance will never run out.

【0019】

Because superoxide anions and peroxide anions both have a powerful oxidizing action, they are able to decompose VOCs

and other harmful chemical substances, and hold promise in applications such as the oxidative decomposition of these harmful chemical substances in the environmental field. Furthermore, the consumed active oxygen (superoxide anions and peroxide anions) is regenerated in the structure of the novel active oxygen developing substance of the present invention, and therefore this substance has the advantage that it can be used indefinitely.

[0020]

[Example]

The present invention will now be described in specific terms by giving examples, but the present invention is not limited in any way by the following examples.

Example 1

0.77 g of unslaked lime (as a calcia source), 1.8 g of alumina sol (as an alumina source; containing 20% Al_2O_3), and 0.21 g of amorphous silica (as a silica source) were weighed out, and water was added to bring the total volume up to 14.6 mL. The mixture (suspension) thus prepared was put in an autoclave with a capacity of 25 mL, and heated for 15 hours at 200°C while being stirred at 25 rpm. The system was then allowed to cool to room temperature, filtered, and dried, which gave hydrogarnet expressed by the compositional

formula $Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8}$. This hydrogarnet was heated for 5 hours at 700°C in an electric furnace under an air atmosphere, which gave $Ca_{12}Al_{10}Si_4O_{35}$ (a novel active oxygen developing substance). Figs. 1 and 2 show the ESR and Raman spectroscopy results at room temperature for the $Ca_{12}Al_{10}Si_4O_{35}$ produced by this method. As discussed above, $Ca_{12}Al_{10}Si_4O_{35}$ was confirmed to include or occlude active oxygen in its structure.

【0021】

Example 2

1.0 g of $Ca_{12}Al_{10}Si_4O_{35}$ that had been molded into pellets with a size of 300 to 500 μm was packed into a quartz glass reaction tube that had been placed in an electric furnace, and the reaction tube temperature was set to the desired temperature between 200 and 900°C. A mixed gas of air and propylene was introduced into the reaction tube at a flux of 100 mL/min. The propylene concentration was 1000 ppm. The outlet gas from the reaction tube was introduced to a gas chromatograph, and the gas was analyzed. No decomposition of propylene was noted between 200 and 375°C, but 2% decomposition was noted at 400°C. The decomposition rate rose along with the reaction temperature, reaching 50% at 500°C, 95% at 550°C, and 100% at over 600°C. The only gases

produced by the decomposition of the propylene were CO_2 and H_2O, indicating that a propylene oxidative decomposition reaction had occurred.

【0022】

Example 3

1.0 g of $Ca_{12}Al_{10}Si_4O_{35}$ that had been molded into pellets with a size of 300 to 500 µm was packed into a quartz glass reaction tube that had been placed in an electric furnace, and the reaction tube temperature was set to the desired temperature between 200 and 900°C. A mixed gas of air and benzene was introduced into the reaction tube at a flux of 100 mL/min. The propylene concentration was 1000 ppm. The outlet gas from the reaction tube was introduced to a gas chromatograph, and the gas was analyzed. No decomposition of benzene was noted between 200 and 400°C, but 3% decomposition was noted at 425°C. The decomposition rate rose along with the reaction temperature, reaching 10% at 450°C, 37% at 500°C, 86% at 550°C, 98% at 600°C, and 100% at over 625°C. The only gases produced by the decomposition of the benzene were CO_2, CO, and H_2O, indicating that a benzene oxidative decomposition reaction had occurred.

【0023】

Example 4

1.0 g of $Ca_{12}Al_{10}Si_4O_{35}$ that had been molded into pellets with a size of 300 to 500 μm was packed into a quartz glass reaction tube that had been placed in an electric furnace, and the reaction tube temperature was set to 600°C. A mixed gas of nitrogen and propylene was introduced into the reaction tube at a flux of 50 mL/min. The propylene concentration was 100 ppm. The outlet gas from the reaction tube was introduced to a gas chromatograph, and the gas was analyzed. The relationship between propylene decomposition rate and reaction time was measured. These results are shown in Fig. 4. The initial decomposition rate was 80%, but this decreased over time, dropping to 0% after 120 minutes, after which no oxidative decomposition of propylene occurred. Fig. 7 shows the Raman spectroscopy results for the active oxygen in $Ca_{12}Al_{10}Si_4O_{35}$ obtained after propylene decomposition in a nitrogen atmosphere at various reaction times. The active oxygen in the structure decreased as the combustion of the propylene proceeded. Furthermore, it was confirmed that the active oxygen was regenerated in the structure by exposing the $Ca_{12}Al_{10}Si_4O_{35}$ that had lost its active oxygen to air at 400°C or higher. It was shown that the active oxygen in the lattices consumed by the oxidation reaction was regenerated by taking in oxygen from the air, allowing the propylene to burn continuously.

【0024】

【Effect of the Invention】

The present invention relates to an aluminosilicate having a zeolite-like structure in which active oxygen (superoxide: O_2^-, peroxide: O_2^{2-}) is encapsulated, that is, a novel active oxygen developing substance. The active oxygen included or occluded in the structure of this substance induces hydrocarbon oxidation reactions (such as epoxidation, complete oxidation, partial oxidation, and coupling), and the novel active oxygen developing substance of the present invention can be utilized in a wide range of technological fields dealing with the environment, energy, the chemical industry (manufacturing process), and so forth.

【0025】

【Brief Description of The Drawings】

【Fig. 1】

Fig. 1 shows the ESR measurement results for $Ca_{12}Al_{10}Si_4O_{35}$ at room temperature;

【Fig. 2】

Fig. 2 shows the results of Raman spectroscopy for $Ca_{12}Al_{10}Si_4O_{35}$ at room temperature;

【Fig. 3】

Fig. 3 shows the crystal structure of $Ca_{12}Al_{10}Si_4O_{35}$;

【Fig. 4】

Fig. 4 shows the relationship between reaction time and the propylene decomposition rate under a nitrogen atmosphere (a) using $Ca_{12}Al_{10}Si_4O_{35}$ as the catalyst (air was introduced (b) 220 minutes after the start of the reaction, the active oxygen consumed in the $Ca_{12}Al_{10}Si_4O_{35}$ was regenerated, and the oxidative decomposition of propylene in a nitrogen atmosphere was recommenced);

【Fig. 5】

Fig. 5 shows the Raman spectroscopy results for $Ca_{12}Al_{10}Si_4O_{35}$ after a propylene decomposition experiment in a nitrogen atmosphere;

【Name of Document】 Abstract

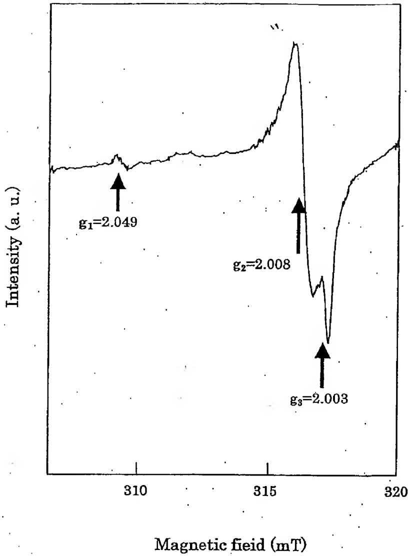
【Summary】

【Subject】 Novel active oxygen developing substance and method thereof are provided.

【Means of solution】 The present invention relates to an active oxygen developing substance composed of an aluminosilicate obtained by heating hydrogarnet as a precursor substance at 700°C or higher; an aluminosilicate catalyst supporting cobalt oxide, produced by supporting cobalt oxide on the surface of the aluminosilicate; a method for manufacturing these.

【Effect】 The active oxygen developing substance of the present invention is useful as a constituent component of oxidation catalysts, solid electrolyte fuel cell electrodes, antimicrobial agents, ion conductors, or the like.

【Figure to be selected】 None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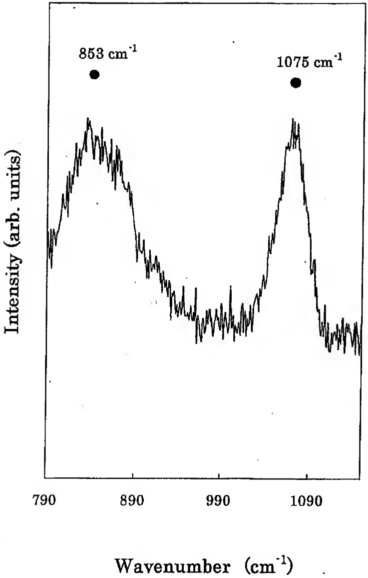
g2=2.008
g3=2.003
Intensity (a. u.)
310
315
320
Magnetic fieid (mT)

Fig 1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1075 cm-1
Intensity (arb. units)
790
890
990
1090
Wavenumber (cm-1)

Fig 2

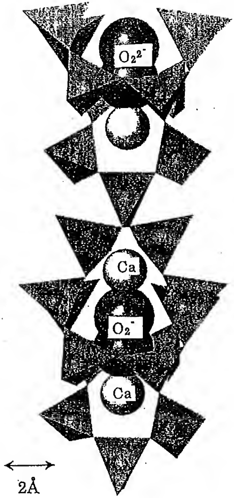

Fig 3

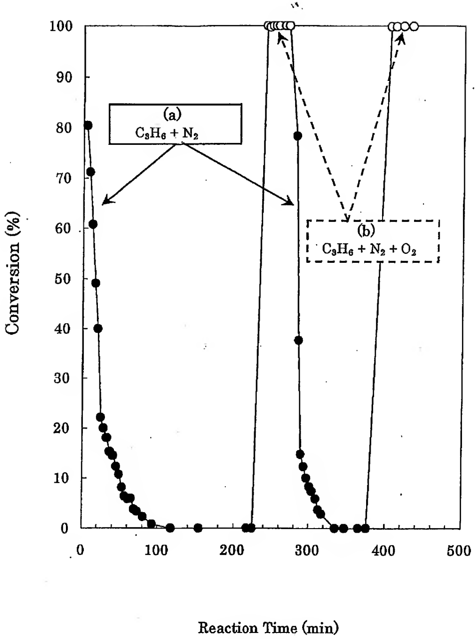
100
90
80
70
60
50
40
30
20
10
0
Conversion (%)
0
100
200
300
400
500
Reaction Time (min)
(a)
$C_3H_6 + N_2$
(b)
$C_3H_6 + N_2 + O_2$

Fig 4

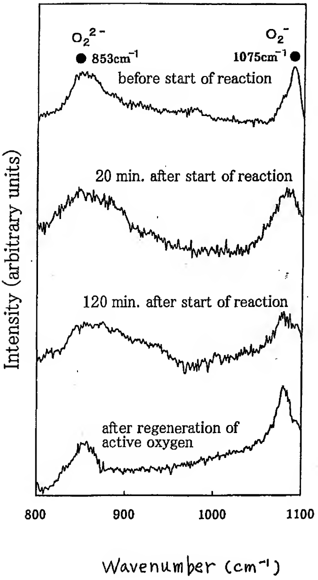
O_2^{2-}
853cm^{-1}
O_2^{-}
1075cm^{-1}
before start of reaction
20 min. after start of reaction
120 min. after start of reaction
after regeneration of
active oxygen
Intensity (arbitrary units)
800
900
1000
1100
Wavenumber (cm^{-1})

Fig. 5